On the localization of tetrahedral aluminum in MCM-22 zeolite

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The distribution of aluminum in MCM-22 zeolite has been studied by ^{27}Al solid-state nuclear magnetic resonance. Three different aluminum species in tetrahedral position were observed. Surface selective dealumination with oxalic acid causes the disappearance of one of the NMR signals at 50.5 ppm. The corresponding species have been attributed to aluminum atoms located in the 12-T large cavities located on the external surface of the zeolite crystals.

Keywords: MCM-22, ^{27}Al 2D-5Q MAS NMR, dealumination

1. Introduction

MCM-22 zeolite is a peculiar solid having a unique and unusual crystal structure [1,2]. The interesting catalytic properties of this zeolite are at the origin of several reports [3,4]. MCM-22 is known to possess two independent multidimensional channel systems, one pore system being composed of two-dimensional sinusoidal channels (delimited by 10 T atoms), the other consisting of large supercages (12 rings) linked by 10-MR windows. Moreover, it has been shown recently that MCM-22 crystallizes as very thin plates, the surface of these plates containing 12-ring pockets. The ratio of surface 12-ring pockets to the total number of 12-ring cages depends on the thickness of the crystal plates since the pores containing these large pockets are oriented perpendicularly to the surface plates [2]. MCM-22 has been characterized using various techniques including solid-state MAS NMR spectroscopy [5–11]. It has been possible to propose the existence of five non-equivalent aluminum sites having chemical shift of 49.0, 53.3, 55.5, 57.5 and 62 ppm [5]. By using quadrupolar nutation ^{27}Al NMR, Kolodziejski et al. [7] were able to distinguish experimentally two different aluminums in tetrahedral coordination at 48.1 and 53.5 ppm. The authors suggested that these two 4-coordinated Al species result from two sets of framework tetrahedral sites, differentiated by their location in small and large atom rings and/or by their structural relation to the two distinct pore systems proposed for this zeolite.

In order to gain more information about the aluminum location, we have reinvestigated this question by using a different approach involving selective surface dealumination [8]. We have selectively dealuminated the surface by treating the MCM-22 zeolite with a 2 N oxalic acid solution at 343 K for 2 h. It is known from the literature that oxalic acid is only able to extract aluminum from large-pore (12-T) and not from medium-pore (10-T) zeolites [8]. The resulting solid was characterized by ^{27}Al NMR, IR spectroscopy (OH vibrations) and catalytic test (hydrocracking of 2,2,4-trimethylpentane (TMC$_5$)) to probe the number of surface acid sites.

2. Experimental

MCM-22 zeolite was synthesized as described in [9]. The Si/Al ratio in the gel was 15 and chemical analysis indicated a similar value in the final solid. As reported earlier, the MCM-22 zeolite was well crystallized, as evidenced by XRD [10].

The total number of acid OH groups vibrating at 3620 cm^{-1} was monitored by using IR spectra recorded on a Vector FTIR Bruker spectrometer. Samples were pressed as small wafers (∼20 mg) and outgassed *in situ* overnight at 723 K before registration of the IR spectrum.

The catalytic tests were run by using a microflow reactor, products and reactant being analyzed by on-line gas chromatography. Tests were performed at atmospheric pressure, $T = 523$ K, $P_{\mathrm{H}_2}/P_{n\mathrm{C}_8}$ being fixed to 60 [10]. The MCM-22 support was loaded with 0.6 wt% Pt and 1.2 wt% Pd and the catalyst was reduced under hydrogen. It has been checked that the catalyst prepared in such a way behaved like a true bifunctional catalyst [10].

NMR spectra were recorded on a Bruker DSX 400 spectrometer operating at 104.2 MHz. Samples were spun at 14 kHz in zirconia rotors using a 4 mm double-bearing probe head. ^{27}Al MAS NMR spectra were obtained using a pulse length of 1 μs ($\pi/6$) and a recycle delay of 1 s. All spectra were recorded with the same number of scans (1000) in order to compare the relative intensities of the signals and to estimate the extent of dealumination after treatment of the zeolite with oxalic acid. ^{27}Al two-dimensional five-quanta (2D-5Q) MAS NMR spectra were recorded using the published pulse sequence [11] with 1024 scans for each free induction decay and a recycle delay of 0.3 s. Eighty time domain real data points were acquired in the indirect dimension and pure-phase spectra were achieved by using the TPPI scheme [12,13]. ^{27}Al chemical shifts were referenced to $Al(H_2O)_6^{3+}$.

3. Results

In table 1 are reported the main characteristics of initial and oxalic acid treated MCM-22. It appears that the acid treatment strongly decreases the number of surface acid sites, as probed by the hydrocracking of TMC_5. For the sample that was treated for 4 h, the remaining number of surface sites is less than 10% of the initial value. Indeed, IR spectroscopy shows that the total number of OH sites vibrating at $\nu_{OH} = 3620$ cm^{-1} is not strongly affected since 92% of the initial acid sites are still present after the surface dealumination treatment.

We will now see what are the modifications observed in the ^{27}Al NMR spectra. The ^{27}Al MAS NMR spectrum of as-synthesized MCM-22 (Si/Al = 15) is composed of two signals at 55.8 and 49 ppm, characteristic of tetrahedral framework aluminum species. Upon calcination, an additional peak is observed at ca. 0 ppm, which results from the presence of extraframework aluminum species. The signal corresponding to 4-coordinated Al species shows a major resonance at 57.8 ppm along with shoulders at ca. 50.5 and 63 ppm. When the calcined material has been treated for 2 h with oxalic acid, the intensity of the shoulder at 50.5 ppm decreases whilst that of the shoulder at 63 ppm increases with respect to the major line. After two consecutive treatments, the spectrum looks to be composed of an asymmetric peak, with maximum intensity at 58 ppm, together with a second signal at 63 ppm. The shoulder at 50.5 ppm, which was clearly evidenced in the spectrum of the calcined material, is not observed anymore. This indicates that a prolonged treatment of calcined MCM-22 with oxalic acid probably modifies the distribution of aluminum atoms in the zeolite framework. A semi-quantitative estimation of the intensity of the NMR signal shows that approximately 22% of the amount of aluminum has been removed.

Table 1
Acidity and catalytic activity in the 2,2,4-trimethylpentane hydrocracking of various MCM-22 zeolites.

MCM-22	Number of acid OH groups[a]	Rate of TMC_5 hydrocracking[b]
Initial	1	1
Treated 2 h with 2 N oxalic acid at 343 K	0.95	0.2
Treated 4 h with 2 N oxalic acid at 343 K	0.92	0.08

[a] Adsorbance of the OH vibration (3620 cm^{-1}) measured by IR spectroscopy after having outgassed the solid for 4 h at 723 K (arbitrary units).

[b] Rate of 2,2,4-trimethylpentane hydrocracking measured at 523 K, $H_2/HC = 60$, the zeolite being loaded with 0.6 wt% Pt and 1.2 wt% Pd. The product of hydrocracking of TMC_5 is isobutane (arbitrary units).

However, the interpretation of ^{27}Al MAS NMR spectra is difficult, essentially because of second-order quadrupolar broadening. One possibility to separate the contributions of aluminum species with different isotropic shifts and quadrupolar constants is to use a two-dimensional five-quanta (2D-5Q) sequence, originally introduced by Frydman et al. [14] and optimized by Fernandez et al. [11] for the study of $S = 5/2$ nuclei. This method provides enhanced resolution as compared with ordinary MAS spectra since the second-order quadrupolar broadening is removed and the chemical shift dispersion is amplified, as it would be in a field approximately five times more intense.

The 2D-5Q MAS NMR spectrum of calcined MCM-22 clearly shows three signals in the tetrahedral region. These signals are not spread along the anisotropy axis A, which indicates a distribution of chemical shifts and quadrupolar constants, resulting from a random location of aluminum in the framework. From the spectrum, it is possible to estimate the isotropic shifts as well as the quadrupolar constants for the three species using the relations:

$$\delta_{\rm iso}(i) = X_2(i) - Q_{\rm iso}(i),$$
$$C_{\rm Q}(i) = \left[X_1(i) - X_2(i)\right]^{1/2} \times 1.3\ \text{MHz},$$

where $Q_{\rm iso}(i) = (4/9)[X_2(i) - X_1(i)]$ is the quadrupolar induced shift and $X_2(i)$ and $X_1(i)$ are the coordinates of the center of gravity of signal (i). Data corresponding to calcined MCM-22 are reported in table 2.

Unverricht et al. [15] reported the existence of four different lines in the tetrahedral region of the ^{27}Al MAS NMR spectrum of calcined MCM-22. However, the deconvolution of the spectrum was made using symmetric Gaussian lines, which did not take into account the possibility of asymmetric NMR signals. More interestingly, the use of ^{27}Al quadrupolar nutation NMR reported by Kolodziejski et al. [7] gave only two peaks at ca. 54 and 47 ppm for a calcined MCM-22 material with Si/Al = 15. There was no evidence for the presence of additional signals at chemical shifts higher than 55 ppm. This shows the power of the multi-quanta technique as compared to MAS and quadrupo-

Table 2
Parameters deduced from ^{27}Al 2D-5Q MAS NMR spectra.

MCM-22	Signal	$\delta_{\rm iso}$ (ppm)	$C_{\rm Q}$ (MHz)
Initial	1	63.95	2.93
	2	59.06	2.13
	3	51.8	2.05
Treated 2 h with 2 N oxalic acid at 343 K	1	63.7	2.83
	2	58.98	2.29
	3	51.85	2.17
Treated 4 h with 2 N oxalic acid at 343 K	1	63.4	2.23
	2	57.7	2.16

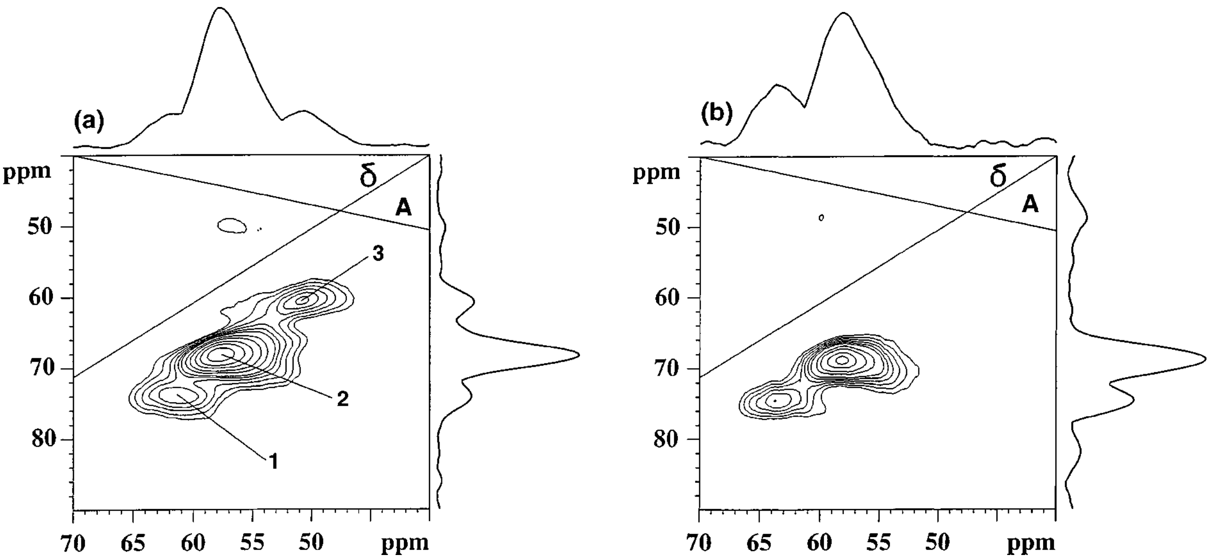

Figure 1. ^{27}Al 2D-5Q MAS NMR spectra of MCM-22 calcined (a) and treated for 4 h with oxalic acid (b).

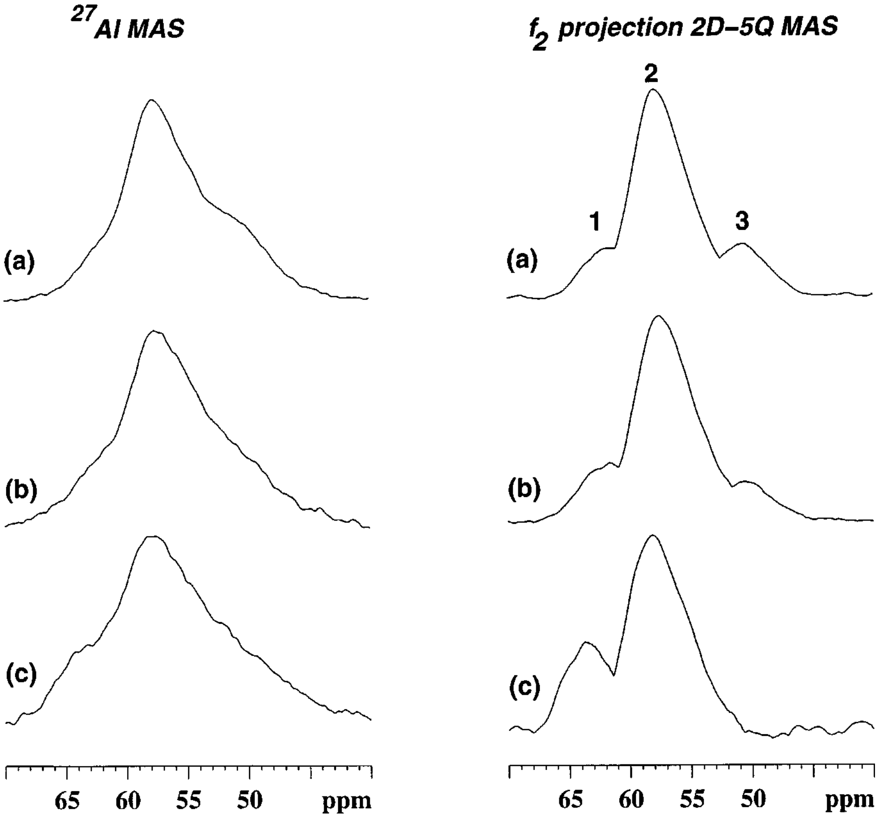

Figure 2. ^{27}Al MAS NMR spectra (left) and projections along the ω_1 dimension of the 2D-5Q MAS NMR spectra (right) of the tetrahedral region of zeolite MCM-22: (a) calcined zeolite, (b) zeolite treated for 2 h with oxalic acid and (c) zeolite treated for 4 h with oxalic acid.

lar nutation NMR to distinguish between aluminum species in the framework of calcined MCM-22. Recently, the existence of three distinct Al signals in calcined MCM-22 has been confirmed by recording the ^{27}Al MAS NMR spectrum in a high static field (17.6 T) [16]. The relative intensities of signals at ca. 61, 56 and 50 ppm were 15 : 62 : 23, in good agreement with those calculated from the projection of the 2D-5Q MAS spectrum, figure 2(a).

The 2D-5Q MAS NMR spectrum of the material treated for 2 h with oxalic acid is similar to that of the calcined zeolite. Nevertheless, we note that the relative intensity of the signal at ca. 50.5 ppm has decreased. After a second treatment, this signal has completely disappeared and the spectrum shows only two lines at 56.7 and 63 ppm. This is particularly evidenced when comparing the f_1 projections of the 2D-5Q spectra. This strongly suggests that oxalic acid preferentially removed one of the aluminum species from the framework of MCM-22.

As discussed above, NMR results clearly indicated the presence of three distinct aluminum sites. Since one of these Al species is disappearing after oxalic acid treatment and since the dealumination procedure used allows only the extraction of Al located on the external surface of the grains and/or in large cavities widely opened on the external surface of the crystals (characterization results are in agreement with such a picture), one can conclude that the ^{27}Al resonance at 50.5 ppm has to be assigned to these aluminum species.

From IR results, one can conclude that nearly 10% of the total OH acid sites are located on the external surface of the MCM-22 crystals in the 12-T pockets. This value is not very different from that measured by Corma et al. [17] by using a bulky base (2,6-di-*tert*-butylpyridine) to probe only acid surface sites. Indeed, the ratio of the surface acid sites to the total number of acid sites will depend on the thickness of the MCM-22 crystals.

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